PHYSICAL REVIEW VOLUME 111, NUMBER 1 JULY 1, 1958

Annihilation of Positrons in Organic Compounds*

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(Received February 3, 1958)

The mean life τ_2 and the fraction I_2 of positrons which decay with a "long" 10^{-9}-sec lifetime have been measured in several organic compounds, most of which are derivatives of benezene. For the long components observed in liquids τ_2 ranges from 1.6×10^{-9} sec to 2.5×10^{-9} sec, whereas I_2 varies from 35% to 4%. A correlation between I_2 and certain properties of the molecules indicates a qualitative explanation of the results.

I. INTRODUCTION

PREVIOUS investigators have found that in some condensed materials, positrons have a complex decay scheme in which part of the positrons decay with a lifetime of about 10^{-10} sec and the remaining ones have a mean life τ_2 of approximately 10^{-9} sec. Bell and Graham[1] suggested that the τ_2 component is due to the formation of triplet positronium which is converted to the singlet state by collision. Lending further support to the hypothesis of positronium formation in condensed media, the addition of small amounts of diphenyl picryl hydrazyl (DPH) to benzene was found to increase the two gamma coincidence counting rate[2] and also to decrease the lifetime of the τ_2 component.[3]

In the earlier work,[4] a value of about 30% was usually reported for the fraction I_2 annihilating by the τ_2 component. More recently, I_2 has been observed to range from ~2% to 53% and evidence has been presented which indicates that the τ_2 component is largely due to decay of triplet positronium by "pickoff" annihilation with bound electrons.[5]

The arrangement, Fig. 1, used in this work to study positron decay schemes, is practically the same as those described earlier.[6] Positrons emitted from Na^{22} are allowed to enter the compound which is to be studied and delayed coincidences are measured between the 1.28-Mev nuclear gamma ray and one of the annihilation quanta, as a function of the artificial delay x in the creation channel. In order that a coincidence be recorded, three pulses must arrive at the triple coincidence circuit within 1 μsec of one another corresponding to (1) a fast (2×10^{-9} sec) coincidence between any two limited pulses, (2) an energy loss in the 1.3-Mev channel scintillator of greater than 0.6 Mev and (3) an energy loss in the 0.5-Mev channel scintillator of greater than 0.2 Mev. The output of the triple coincidence circuit is fed to the scaler unless a pulse arrives from the 0.5-Mev channel amplifier corresponding to an energy loss in excess of 0.4 Mev. The stability of the assembly can probably be attributed to the use of negative feedback throughout the apparatus and a wide-band amplifier before the biased diode. Calibration of the helical delay line was accomplished by shorting one end and measuring the distance between nodes of a standing wave.

II. DATA ANALYSIS

In order to measure mean lives τ_1 which are short compared to the resolution of the fast coincidence arrangement, and also in order to determine the fraction I_2 which annihilates with a long mean life τ_2, it is necessary to know the resolution curve $P(x)$. An approximation to the true resolution curve was obtained by using the gamma rays of Co^{60} in the manner suggested by Gerholm.[7] During the experiment, a Co^{60} resolution curve was taken every ten days. Seven such curves were taken and the centroid of each curve was calculated in order to find "zero" relative delay. Over a period of two months, there was no evidence of a long-

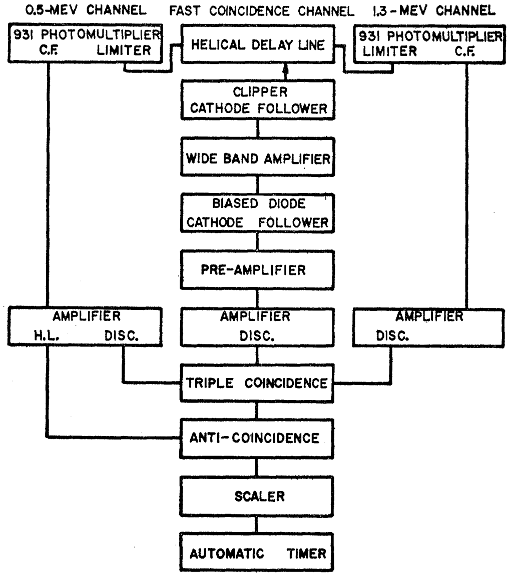

FIG. 1. Block diagram of the delayed coincidence arrangement used to study positron decay schemes in condensed materials.

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* This research was supported in part by the U. S. Air Force Office of Scientific Research of the Air Research and Development Command.

† Portion of thesis comprising partial fulfillment of the requirements for the Ph.D. degree in physics at the University of Texas.

[1] R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).

[2] T. A. Pond, Phys. Rev. **93**, 478 (1954).

[3] S. Berko and A. J. Zuchelli, Phys. Rev. **102**, 724 (1956).

[4] S. Berko and F. L. Hereford, Revs. Modern Phys. **28**, 299 (1956).

[5] R. E. Green and R. E. Bell, Can. J. Phys. **35**, 398 (1957).

[6] Bell, Graham, and Petch, Can. J. Phys. **30**, 35 (1952).

[7] T. R. Gerholm, Arkiv Fysik **10**, 535 (1956).

TABLE I. Experimental results for positrons annihilating in organic compounds.[a]

Compound		I_2%	τ_2 (10^{-9} sec)	τ_1 (10^{-10} sec)	Description of sample
C_6H_6	Benzene	35±2	2.1±0.1		liquid
$(C_6H_5)F$	Fluorobenzene	24±2	1.8±0.1		liquid
$(C_6H_5)Cl$	Chlorobenzene	14±2	1.6±0.1		liquid
$(C_6H_5)Br$	Bromobenzene	6±2	1.6±0.2		liquid
$(C_6H_5)I$	Iodobenzene	4±2	1.6±0.3		liquid
$(C_6H_5)CH_2Cl$	α-Chlorotoluene	unobserved		2.1±1.5	liquid
$(C_6H_5)CH_3$	Toluene	26±2	1.9±0.1		liquid
$(C_6H_5)C_2H_5$	Ethylbenzene	20±1	2.2±0.1		liquid
$(C_6H_5)C_3H_7$	Isopropylbenzene	31±2	1.9±0.1		liquid
$(C_6H_5)NH_2$	Aniline	25±2	1.7±0.1		liquid
$Cl(C_6H_4)Cl$	*p*-dichlorobenzene	unobserved		2.6±0.4	powder
$Cl(C_6H_4)Cl$	*o*-dichlorobenzene	unobserved		2.9±1.7	liquid
$NO_2(C_6H_4)NO_2$	*p*-dinitrobenzene	unobserved		2.2±0.4	powder
$CH_3(C_6H_4)CH_3$	*p*-xylene	24±2	2.1±0.1		liquid
$CH_3(C_6H_4)CH_3$	*m*-xylene	19±1	2.2±0.1		liquid
$CH_3(C_6H_4)CH_3$	*o*-xylene	12±1	2.0±0.1		liquid
C_5H_{12}	*n*-pentane	26±2	2.5±0.1		liquid
CCl_4	Carbon tetrachloride	unobserved		2.5±1.5	liquid
C_6H_{12}	Cyclohexane	30±2	2.1±0.1		liquid
C_6H_{10}	Cyclohexene	27±2	2.4±0.1		liquid
$C_{14}H_{10}$	Anthracene	unobserved		2.3±0.4	crystal
$C_{14}H_{10}$	Anthracene	unobserved		2.9±0.4	powder
$C_{14}H_{10}$	Phenanthrene	14±2	1.2±0.1		powder

[a] τ_1 is the mean life of the short component; τ_2 is the mean life of the long component; I_2 is the fraction of positrons which annihilate with mean life τ_2.

term drift in centroid position. The probable error was computed from deviations and found to be about 10^{-11} sec.

Positrons entered the liquid samples by passing through 0.0002-in. aluminum foil windows. Because of good source geometry, it was unnecessary to correct for annihilation in any part of the sample holder other than the thin windows. The fraction r of positrons annihilating in the foils was determined in the way now described. A delayed coincidence curve $f_t(x)$ was taken for Teflon; next, another curve $F_t(x)$ was taken with the same Teflon sample covered with 0.0002-in. aluminum foil. For points which lie on the exponential tails, $F_t(x)/f_t(x)=1-r$. From this equation r was calculated for ten sets of points and the error in r was computed from deviations. A value of $r=(18.2\pm5.0)\%$ was obtained. This result was checked by computing the percentage of τ_2 component for the two samples and the two values of r were found to agree to one place in the third figure.

As a precaution against short-term drift, two complete sets of data were obtained for each sample studied. Since between 9 and 12 hours were required to accumulate a single curve, it generally took two days to study one compound. To reduce evaporation, the tanks containing the liquid samples were sealed with threaded Teflon plugs. For most of the liquids, about 15% evaporated in a period of 24 hours. This effect was not serious because the tanks were refilled between runs and points on the exponential tail and peak were usually completed within six hours after filling.

After normalizing the data and correcting for annihilation in the foils, the N points on an exponential tail were given a least squares fit. Since, in regions where[8] $f(x)\gg P(x)$,

$$-\frac{1}{\tau_2}=\frac{d\ln f(x)}{dx}=\frac{dp(x)}{dx},$$

the procedure followed was to determine τ_2 and b, where

$$y=-(1/\tau_2)x+b,$$

such that $\sum[y(x_n)-p(x_n)]^2$ is a minimum. This requirement leads to

$$\tau_2=-\sum(x_n-x_b)^2/\sum[p(x_n)(x_n-x_b)],$$

$$b=(1/N)\sum p(x_n),$$

where $x_b=(1/N)\sum x_n$, and the summations are carried out over the N points on the exponential tail. Having determined τ_2, the normalized delayed coincidence curve that would have been obtained if all the positrons had decayed with a mean life τ_2 can be computed[8] from

$$f_2(x)=\lambda e^{-\lambda x}\int_{-\infty}^{x}e^{\lambda t}P(t)dt;\quad \lambda=\frac{1}{\tau_2}.$$

The quantity $b'=\ln f_2(x_b)$ is of interest since the

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[8] T. D. Newton, Phys. Rev. 78, 490 (1950).

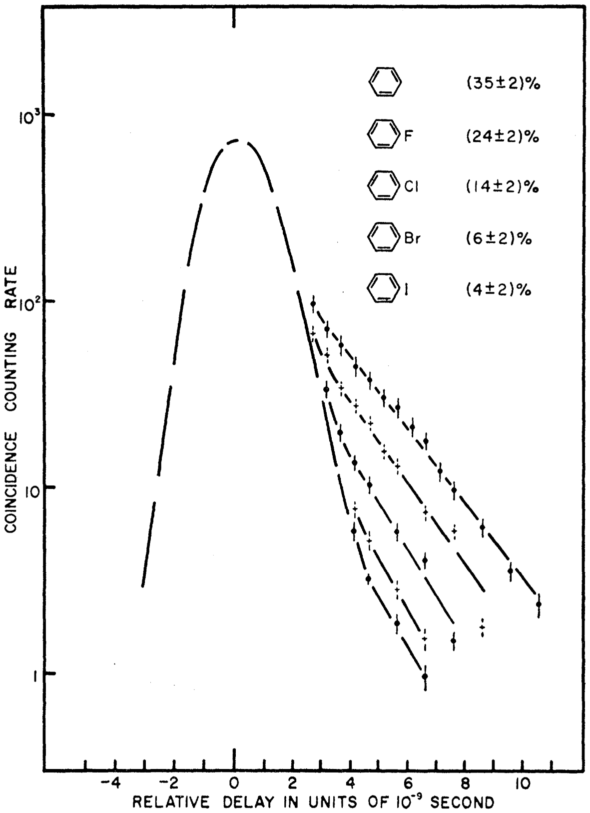

FIG. 2. Delayed coincidence curves for benzene and its halogen derivatives, showing the reduction of I_2 as the size of the halogen is increased.

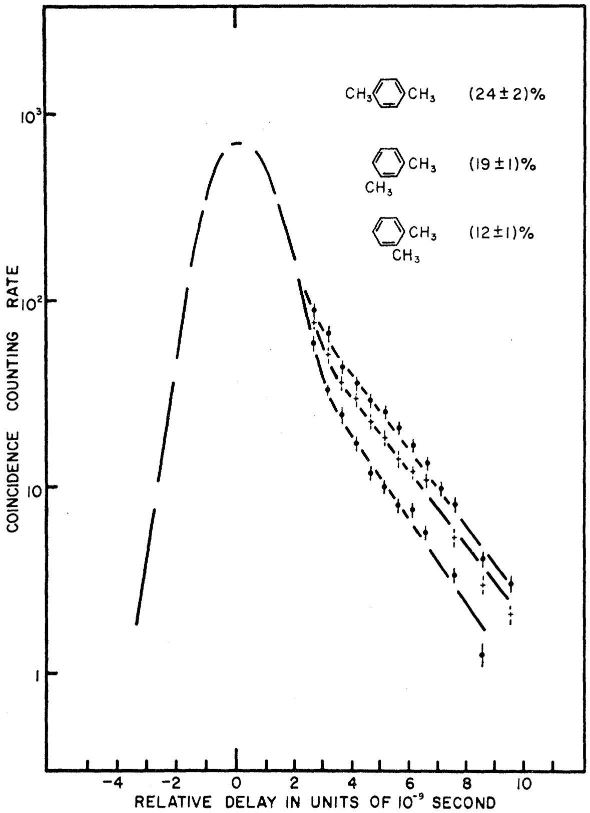

FIG. 3. Delayed coincidence curves for the xylenes. The structure of the molecule and the corresponding value of I_2 is indicated.

equation

$$I_2=e^{b-b'}=e^b/f_2(x_b)$$

gives the fraction which decayed with a mean life τ_2.

The mean life τ_1 of the short component was computed from the centroid shift for those compounds in which no long component was observed. The probable error in the measurement of τ_1 is much larger for liquids than for solids due to the uncertainty in the correction for annihilation in aluminum. In fact, the error in τ_1 for liquids becomes so large when a sizable long component must be subtracted out, that very little information could be obtained by calculating τ_1 for the two component curves obtained.

The probable errors in τ_1, τ_2, and I_2 were computed from probable errors in $f(x)$, x, and $P(x)$. The approach used to calculate τ_2 and I_2 provides a convenient method for computing probable errors. Those errors quoted in Table I therefore represent calculations based on a statistical picture, taking into account the uncertainty in the correction for annihilation in the aluminum windows, but do not account for such systematic errors as, for example, the failure of Co^{60} to give a perfect resolution curve or drift in the electronic equipment. It is felt that the errors indicated give a reliable account of the accuracy of one measurement relative to another; however, the absolute values of τ_1, τ_2, and I_2 may be off by as much as 2×10^{-10} sec, 0.5×10^{-9} sec, and 5%, respectively.

Since there were several compounds studied in which no long component was observed, an unrefined empirical approach was employed to determine the conditions on I_2 and τ_2 such that a long component should have been detected with the apparatus used. It was found that, at least to a fair approximation, a long component should have been observed if

$$I_2>(35\%)/(22.6-20.0/\tau_2) \quad \text{for} \quad 1\leq\tau_2\leq3,$$

where τ_2 is measured in units of 10^{-9} sec. The smallest value of τ_2 measured for any of the liquids studied was 1.6×10^{-9} sec; thus, it is probable that in those liquids for which no long component was observed, I_2 is less than 4%.

III. RESULTS

The results obtained for positrons annihilating in organic compounds are summarized in Table I. The compounds are arranged in groups of related molecules and delayed coincidence curves for two of the more interesting families are shown in Figs. 2 and 3.

For the halogen derivatives of benzene, I_2 shows a remarkable dependence on the size of the halogen ion.

There is at least qualitative agreement with the results obtained by electron impact experiments (Table II) in which the fraction of collisions involving the removal of one electron was found to decrease as the size of the halogen was increased. In accord with this picture, there can be found a correlation between the observed I_2 and the force constants for carbon-halogen bond stretching. Carbon-halogen (C-X) stretching constants have been calculated for the methyl halides CH_3X; typical values are 5.96, 3.64, 3.13, and 2.65×10^{-5} dynes/cm in the order of increasing halogen size.[9] This would seem to suggest that positronium formation is more probable in liquids whose molecules are less likely to rupture on collision with an electron. For most of the liquids studied, this oversimplified approach seems to give a surprisingly consistent correlation between I_2 and the force constant for the weakest bond in the molecule. For example, it predicts that I_2 goes in decreasing order for benzene, toluene, chlorobenzene, and α-chlorotoluene. There are certain exceptions to the rule, however. A larger I_2 was measured in benzene than in fluorobenzene, although the force constant for carbon-fluorine bond stretching is greater than that of a carbon-hydrogen bond. Also, since the force constant for double bond carbon-carbon stretching is greater than that of a carbon-carbon single bond, cyclohexene would be expected to give a larger I_2 than cyclohexane. These two exceptions are alike in that each concerns the resulting decrease in I_2 when a symmetric molecule is altered in such a way that (1) the bonding should be stronger and (2) the new molecule is asymmetric. Perhaps this implies that the distribution of charge in the molecule should be considered.

For the compounds studied, there appears to be no dependence of I_2 on either the ionization potential or the dipole moment of the molecule. On the other hand, a concentration of negative charge might reduce I_2 by causing more positrons to annihilate with bound electrons. This picture can be used to explain the results for fluorobenzene, cyclohexene, and even the xylenes.

When one of the hydrogen atoms of benzene is replaced with F, Cl, Br, I, or NO_2, the electron density on on the ring is decreased and the group added becomes the negative end of an electric dipole. The addition of CH_3, C_2H_5, C_3H_7, or NH_2 has the effect of increasing the electron density on the ring; consequently, the group added to the ring becomes the positive end of the dipole. According to this picture, the addition of a group of the first kind would be expected to have more of an effect than the addition of a group of the second kind, because in the first case the negative charge is more concentrated. Similarly, o-xylene should give a smaller I_2 than p-xylene since the negative charge on the ring is more localized for o-xylene than it is for p-xylene.

Table II. Electron impact data reported by Momigny.[a] The compounds were bombarded with electrons of 70 ev energy and the fragments were analyzed with a mass spectrometer.

Compound $(C_6H_5)X$	Relative total ionization	Fraction of total ionization $(C_6H_5)X^+$	$(C_6H_5)^+$	X^+
$(C_6H_5)F$	100	42.12	0.66	0.05
$(C_6H_5)Cl$	96	37.19	15.91	0.58
$(C_6H_5)Br$	91	31.61	24.17	1.68
$(C_6H_5)I$	102	28.55	24.25	3.46

[a] J. Momigny, Bull. soc. chim. Belges **64**, 144 (1955) [Chem. Abstracts **49**, 13767g (1955)].

The above interpretation is similar to the one offered by Green and Bell[5] to explain the decrease of I_2 in water upon the addition of NO_3^- and NO_2^- ions. Unfortunately, force constants and electron impact data are not available for the xylenes and so it is impossible at this time to say whether the data for these compounds could be explained in terms of the strength of the bonds between the CH_3 groups and the ring.

A long component was detected in only one of the solids studied. This could be due to the fact that, in general, τ_2 seems to be shorter for solids than for liquids, making detection of a long component more difficult. Since long components have been observed in benzene, naphthalene, and phenanthrene, it is interesting that no long component was detected in anthracene. One possible explanation lies in the variation of melting points for these substances. It has been found that for ice and Teflon[1] τ_2 decreases as the temperature of the sample is lowered. Anthracene has a much higher melting point than benzene, naphthalene, or phenanthrene and, hence, it is frozen harder at room temperature. It is likely, therefore, that τ_2 for anthracene is too short to be observed with the present apparatus. The difference in τ_1, measured for solid anthracene in the powdered and crystalline forms, is attributed to the difference in density.

In conclusion, it might be said that I_2 has been observed to vary over a fairly wide range for annihilation in compounds which are physically and chemically similar. Furthermore, correlation between I_2 and various properties of the molecules suggest that this approach might be used as a method for investigating molecular structure.

ACKNOWLEDGMENTS

The authors wish to thank Mr. John Unik for pointing out the electron impact data, Dr. W. W. Robertson and Dr. Richard Fuchs for suggesting and furnishing some of the compounds, Mr. John Ashe for his assistance in many phases of the work, and Mr. Felix Castillo Jiménez for discussions of the various interpretations of the results.

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[9] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, 1946), Vol. 2, p. 193; A. E. Remick, *Electronic Interpretations of Organic Chemistry* (John Wiley and Sons, Inc., New York, 1946), p. 171.